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## MATERIAL ASPECTS OF HISTORIC FINE CERAMICS

The paper outlines the material and technological aspects of fine (whiteware) ceramics. Particular attention has been paid to the professional nomenclature of fine aluminosilicate ceramics as used in the past and today. Attention was drawn to this mostly overlooked and poorly studied problem. The reason for the durability problems of some semi-vitreous porcelain and faience materials has been explained. The microstructures of porcelain materials – historic as well as contemporary – have been presented in comparative terms, including the technical material, with a distinction and analysis of the basic phases that build up the shard. Generally similar parameters of microstructure and phase composition were found for all tested materials.

*Keywords:* historic faience; semi-vitreous porcelain; historic porcelain; microscopic analysis; microstructure of ceramic shard

### 1. Introduction

The process of making pottery has a tradition dating back several thousand years. Many years of research indicate that the oldest ceramic vessels appeared at the end of the Palaeolithic. Thus, at the same time or even earlier than the beginnings of agriculture and farming [1]. The technology of making pottery is therefore one of the oldest human technologies – after the preparation of food and clothing. Its mastery was due to the readily available raw materials such as plastic clays, sand and the ability to obtain high temperatures in the fire and special kilns for firing ceramic vessels.

It should be noted that from the beginning of its history, ceramics has sought to have an artistic character. Thanks to this, the forms of the wares and the ways of decorating the vessels form one of the bases for separating and defining archaeological cultures. Also, the emergence of one of the oldest production devices in the history of mankind – the potter's wheel – is associated with ceramics (Mesopotamia late 4th millennium BC) [2]. There is also an opinion that the technology of obtaining metals from ores originates from the experience of potters [3]. Ceramic vessels were fired from clays with a high content of metal compounds.

Furthermore, it should be added that such a rich ceramic tradition impinges on the way the early modern period ceramics

have been treated by scholars of cultural and art history. Contrary to appearances, old pottery and the oldest Chinese porcelain have been studied to a markedly greater extent than European ceramics of the last five centuries [4]. The research dealt with the microstructure, the components that build up the shard, the texture and the physico-chemical properties. Also, the glaze and pigment compositions of Chinese porcelain are often better known than the recipes of European manufactures [5]. The decoration technique of ancient Greek vases and the composition of the decorative coatings have been studied for many years and are well described [6,7]. At the same time, the role of Ehrenfried Walther von Tschirnhaus, the now recognised co-creator of European hard porcelain [8,9], has been diminished or even overlooked until recently. Also the history of manufactories and factories producing faience in our lands is relatively little known and no intensive research has been carried out in this direction. Several years of efforts to start a museum of ceramics in Koło (Greater Poland), which were once carried out, have not been successful. Despite the considerable advancement of work and involvement of social initiative [10].

The aforementioned certain paucity of in-depth studies of modern ceramics and the orientation of the work more towards artistic qualities than towards the technical properties of the shard have resulted in inconsistencies in the nomenclature of fine ceramics. Furthermore, material issues are generally

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poorly known among art historians studying ceramics. Hence, it is the material aspects of fine ceramics that are presented in this paper.

## 2. The nomenclature of fine ceramics in the context of the shard structure

Despite years of research and the use of modern methods, the complexity of the microstructure and texture of aluminosilicate ceramics makes proper nomenclature difficult. Even in the case of respected and professional sources there are inaccuracies and inconsistencies [8]. It seems obvious that the material structure of the shard should be treated as the first and essential criterion for recognising and defining the researched historic object. The way of making and decoration is just subsequent research issue. Thus, for the art historian, material properties and technological aspects should form the basis for further considerations, such as typology of shape and decoration, signature research, etc.

After many years of research, in collaboration with E.W. von Tschirnhaus and probably a larger team of collaborators, J.F. Böttger developed in laboratory the first realizable porcelain recipe in early 1708 [9]. More than a year, however, took working out the procedure to obtain a white ceramic shard, corresponding in appearance to what was thought to be Chinese porcelain. The porcelain manufactory was founded in mid-1710 at the Albrechtsburg Castle in Meissen (Kursächsische Manufaktur). Elector of Saxony Friedrich Augustus I (king Augustus II the Strong) thus became the first ruler in Europe to own a porcelain factory [11].

It is now believed that it was originally calcium porcelain [3,12]. Feldspar flux was not used until 1720. J.F. Böttger's recipe, elaborated on the basis of many years of experience, was based on the use of the so-called white earth "Schnorsche Erde" from Auge, in composition with quartz and alabaster flux, exchanged over time for feldspar. The raw material composition, which remains valid today, contained 50% white earth, 25% quartz and 25% flux. The white earth from Auge was a white after firing kaolinitic clay, hence the described composition corresponds to the classic set of so-called hard porcelain [3,9].

Hard porcelain – i.e. high-sintered porcelain – is usually fired within the scope of 1380-1410°C, using kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), potassium feldspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) and quartz ( $\text{SiO}_2$ ). The process is performed according to a firing schedule (changes in firing temperature over time), adapted to the reactions occurring during the thermal treatment. This ensures that a material with the right physical (technical) and aesthetic properties is obtained. Variations in raw material composition have a significant impact on the changes in properties related to the quantitative ratio of crystalline and glass phases that result from firing [13]. Porcelain is a multi-phase material with an unstable equilibrium between the phases. Small changes in composition and/or technology result in significant changes in the properties of the material. Relics of raw materials and reaction

products between them, with the participation of gases (burning atmosphere), remain in its microstructure.

The science of ceramic processes is said to be "stopped reactions chemistry". Thus, starting from a raw materials set that undergoes complete vitrification in the firing process at very high temperatures, it is possible to obtain any transition state by stopping the reactions. This can be achieved by limiting the temperature and firing time. This fact makes the boundaries between the different types of ceramics blurred. This is all the more so because a number of minerals, that enter the raw material composition, among which the clay minerals in particular (kaolins and plastic clays), have specific properties depending on the deposit.

According to the proportion of clay raw materials, feldspar fluxes and quartz, and the progress of the reaction during the sintering process, different types of fine aluminosilicate ceramics can be obtained. It is believed that the structure of the shard of such ceramics can be classified according to the amount of vitreous phase formed after firing [3,14]. With increasing firing temperature (and time), the "degree of maturity" of a series of fine aluminosilicate materials increases. With a similar raw materials composition, typical of hard porcelain (50% kaolinite, 25% feldspar and 25% quartz), there are obtained successively:

Faience	15-25% glassy phase,
semi-vitreous porcelain	20-45% glassy phase,
porcelain	40-65% glassy phase,
overheated porcelain	more than 65% glassy phase,
glass	100% glassy phase.

As the proportion of the glassy phase in the fired product increases – the open porosity decreases, disappearing completely at 40-65% vitreous phase content. However, with a further increase in the amount of this phase – when firing at a higher temperature – there takes place a swelling effect and an increase in porosity. The alloy begins to release nitrogen, which was contained in the feldspars during their formation – the cooling of the molten magma [3]. The nitrogen content varies – depending on the geological origin. The effect is important, however, as isolated pores form in the cooled feldspar alloy, reducing technical and usage parameters (quality) of the material.

Particularly noteworthy is a type of ceramic that is intermediate – between faience and porcelain (or stoneware) – called semi-vitreous porcelain. The open porosity of this type of shard is small – resulting from the high amount of vitreous phase – but nevertheless causes the lack of translucency of the product. The name "semi-vitreous porcelain – *półporcelana*", which in Poland is called *porcelit*, is a relatively new term and its history dates back to the second quarter of the 19th century. In Polish territory the term "*półporcelana*" was used very rarely. Nevertheless, Joseph Freudenreich – the founder of the factory in Koło (1842) specified in this way the factory's products – both in documents and on the official round seal [8]. Currently, these products are most often described as faience. This is despite the fact that they have a much more sintered and compacted, low-open-porosity type of shard – typically semi-vitreous porcelain. The shards of the wares of various other faience's manufactures "*fajansjarnie*" were of a similar nature. In view of the technological difficulties

of the time in making porcelain from insufficiently high-quality raw materials, efforts were made to at least approximate the properties of the products to porcelain.

One of applied methods was to add ground quartz powder to the raw materials composition, the residue of which is present in some old shards, thought to be faience. However, this quartz was too coarsely ground and, despite use of calcium mineralisers (fluxes), did not melt properly. This was due to the firing temperature being too low. It was not possible to raise the temperature, because with the type of clays used in the composition, it would cause the vessels to deform. Meanwhile, quartz grains are subject to volume decrease of 2.4% during the cooling of the fired objects (polymorphic transformation of  $\beta$ -quartz in  $\alpha$ -quartz at 573°C). As a consequence, stresses develop in the micro-areas surrounding the quartz grains, which lead to mechanical weakening of the shard and can be an important source of ageing processes [15]. Quartz stresses caused that products with coarsely ground quartz were unstable.

Regardless of attempts to produce a material with properties as close as possible to those of porcelain, wares from unsuccessful attempts to obtain porcelain, as well as so-called “misfired porcelain” were described as faience vessels. The latter wares, underburned due to a lower vitreous phase content and the presence of open pores, lacked the characteristic porcelain features – shell fracture, translucency and a specific sound when struck. When fired finally, the white wares were probably decorated less carefully and, together with the defective vessels, sold at the price of faience. The aforementioned quartz stresses in the underburned shards caused rapid destruction of these so-called faience vessels. This explains the fact that no faience wares from Korzec manufacture have survived to our times [16]. Highly praised by deputy Jacek Jeziński at the seym proceedings in 1790 – as superior to English ones – unlike the latter, they did not even survive to the First World War. Porcelain wares from Korzec contain coarse residual quartz [3]. When underburned, quartz in this form was particularly damaging and caused relatively rapid cracking of the shard. The unexplained destruction of various other ceramic vessels, such as the remnants left by Michael de Mezer, is also known from documents [16]. In the same way that Korzec faience has not survived, the faience of several other manufactures is also unknown, despite documented and even long-term production.

### 3. Studies of microstructure of fine ceramics' shards

Microscopic tests of samples from fragments of three historic porcelain vessels from the 19th century and perhaps from the turn of the 19th/20th century were carried out years ago, but the results of these studies have not been published. As part of the preparation of this work, an in-depth analysis and interpretation of the results obtained at that time was carried out. Moreover, comparative tests were performed on a typical sample of contemporary porcelain of foreign production and a sample of (electro)technical porcelain type C 110 (quartz material) [17, 18]

of domestic production. It should be noted that the composition of raw materials of insulator porcelain was similar to a typical, traditional composition of the table whiteware.

In order to carry out microscopic examinations, microsections had to be performed using a special delicate procedure. During the preparation of microsections – it was priority to minimize the impact of mechanical processing on the microstructure of the material. This was particularly important in the case of the material of historical artefacts. Samples planned for tests were cut out with the use of a diamond blade saw with 30  $\mu\text{m}$  grain size. The surfaces for tests (microsections) were exposed on the samples by a special procedure. They were cut with the use of a jigsaw, with a working powder with a grain size of 10  $\mu\text{m}$  – in oil suspension. Prepared in this way samples were flooded in epoxy resin and then ground on abrasive paper with a grain size of 1000. The next stage was polishing on diamond pastes with a grain size in the range of 1  $\div$  0.25  $\mu\text{m}$ . Ultimate polishing was conducted using colloidal silica – 90 nm. After the removal of the resin covering, there was removed the material layer with a thickness of several dozen micrometres. Finally the samples were washed in water solutions of micellar liquids in strong acoustic fields.

Identification of the shard-building phases was made using scanning electron microscopy (SEM) and optical microscopy (OM). The latter technique was used primarily for the quantitative assessment of individual phases and the homogeneity of their distribution in the shard. There were used Akashi ABT-55 and JEDL JSM-6460 LV scanning electron microscopes, with the use of high vacuum and without sputtering the surface of the samples, as well as an optical microscope equipped with a computer image analyser by CLEMEX. In order to better visualize individual grains and precipitates, some of the tested samples were etched with 10% HF acid for 15 seconds or longer – if necessary.

The first of the tested materials was a sample taken from a piece of porcelain of an unknown manufacturer. The dish (plate) from which the fragment came was dated to the beginning of the 19th century. The SEM image of the material microstructure is shown in Figs. 1 and 2.

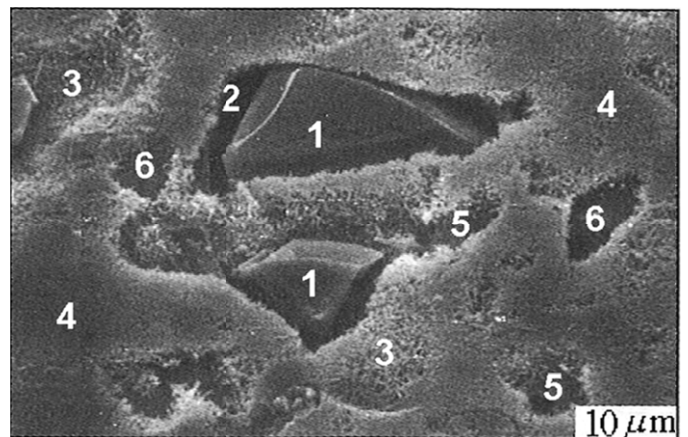


Fig. 1. SEM image of the porcelain microstructure of an unknown manufacturer from the beginning of the 19th century. The following are visible: 1 – quartz grains, 2 – peripheral crack of a quartz grain, 3 – precipitates of secondary mullite needles, 4 – glassy matrix containing scaly primary mullite, 5 – pores, 6 – chipped off small quartz grains

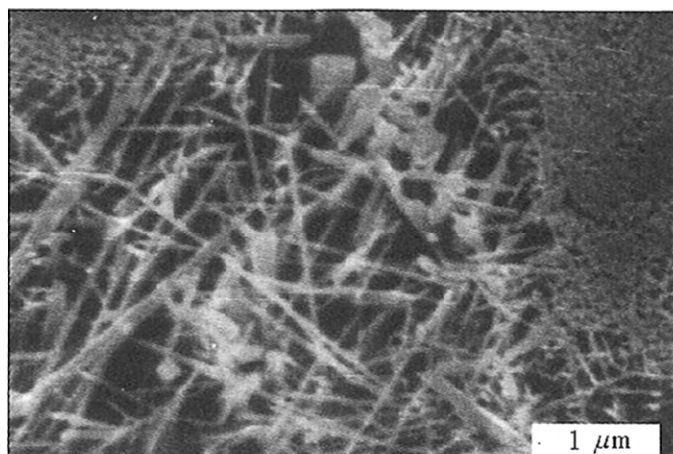


Fig. 2. SEM image of the porcelain microstructure of an unknown manufacturer from the beginning of the 19th century, at high magnification. An area of needle-shaped crystals of secondary mullite precipitate, surrounded by the glassy matrix is visible

The microscopic phase analysis of the porcelain sample dated from the beginning of the 19th century revealed generally acceptable homogeneity in micro scale. The content of residual quartz was equal to about 13%. Dominated fraction of the size of  $5 \div 30 \mu\text{m}$ , but also a significant portion accounted the relics of larger size (max.  $120 \mu\text{m}$ ). Part of quartz relics contained peripheral cracks and was insufficiently connected with matrix. The glass and mullite phases constituted about 80%. The content of the mullite phase could not be accurately determined, especially in the case of primary mullite. However, secondary mullite precipitates accounted for around 20%. Precipitates were most frequently between 10 and  $40 \mu\text{m}$ , and were very well connected with the glassy phase. The porosity was correct – about 7%. The pores were small, typically below  $10 \mu\text{m}$  (max.  $20 \mu\text{m}$ ). The content of the glassy phase in the material can be estimated to be about 60%. The degree of sintering of the material is medium. Needle secondary mullite is present in a typical amount, and porosity is also typical, but most of the quartz grains are angular in shape and show poor melting.

The second examined material was porcelain from a fragment of a tableware, which dates back to the 19th century and cannot be dated more precisely. The manufacturer is also unknown, but it is probably porcelain from a German producer. Images of the material microstructure are shown in Figs. 3 (SEM) and 4 (OM). Already the initial examination of the images indicated a low sintering degree of the porcelain, which can be even described as slightly underburned.

The microscopic phase analysis of 19th century porcelain sample showed fairly good homogeneity in micro scales. The content of quartz was equal to about 16%. A significant part of the quartz grains had chipped off fragments. A lot of internal cracks of the quartz relics was observed. The grains were mostly complex in shape and showed poor melting. This was also indicated by their angular shape. The quartz grains had a very different size – usually several tens of micrometres ( $10 \div 90 \mu\text{m}$ ), but the largest of them reached  $130 \mu\text{m}$ . Part of quartz relics was

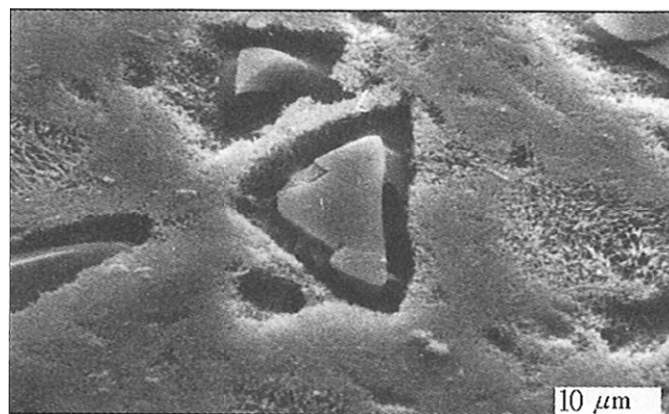


Fig. 3. SEM image of the porcelain microstructure of an unknown (German?) manufacturer from the 19th century. A small angular grains, with rims from molten  $\text{SiO}_2$ , black pores as well as needle secondary mullite precipitates are visible

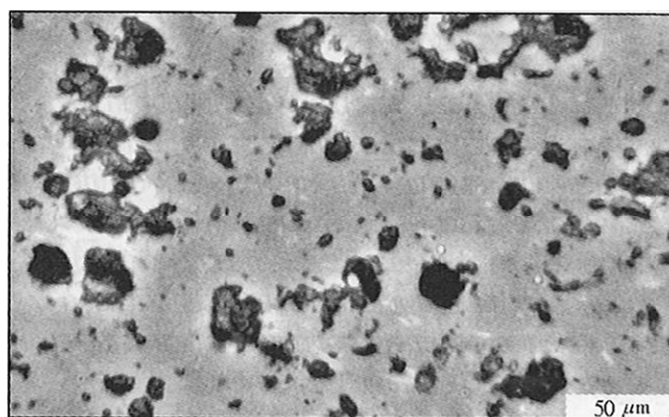


Fig. 4. OM image of the porcelain microstructure of an unknown (German?) manufacturer from the 19th century. Gray quartz grains, sometimes with chipped off fragments and black pores on the background of glassy-mullite matrix are visible

insufficiently connected with matrix and share of them fell out during the preparation of the microsection of the old porcelain sample. In the vicinity of some quartz grains, small cracks passing into the material matrix were observed. There were visible precipitates of needle secondary mullite, which could be estimated at around 15% of the material. Precipitates were relatively small – mostly between  $10\text{--}20 \mu\text{m}$ , but very well connected with the glassy phase. Needle crystals of secondary mullite were small and poorly developed. The content of the primary mullite could not be determined. The porosity of the porcelain was about 8%, and calculated average pore size value equalled  $5.4 \mu\text{m}$ . The content of the glassy-mullite matrix in the porcelain amounted to about 75% – including less than 60% of glass.

The images of the material's microstructure and its parameters indicate a low sintering degree, even slight underburning. What is also noteworthy is the strong cracking of most quartz grains, usually of a complex shape and a low degree of melting. A significant degree of damage in the quartz phase indicate clear aging processes related to quartz stresses and intensified by some underburning of the material. It should be emphasized,

however, that only small number of cracks extending from the quartz boundaries into the matrix were observed.

Another of the examined materials was porcelain from a fragment of a tableware (small plate), which comes from the late 19th century or the turn of the 19th/20th century. The manufacturer is also unknown, but it is probably Russian-made porcelain. Images of the material microstructure – SEM and OM – are shown in Figs. 5 and 6. Unlike the previous material, the examination of microscopic images indicated a high sintering degree or even a slight overheating of the shard.

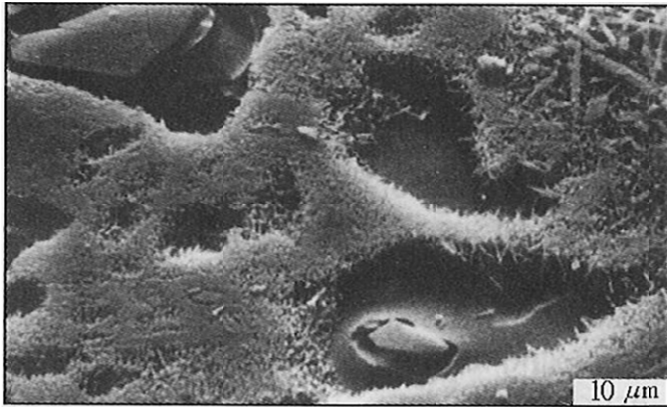


Fig. 5. SEM image of the porcelain microstructure of an unknown, probably Russian manufacturer from the turn of the 19th and 20th centuries. Melted partly and entirely quartz grains as well as matrix with numerous needle crystals of secondary mullite and small pores are visible. In the upper right corner the precipitate of secondary mullite is seen

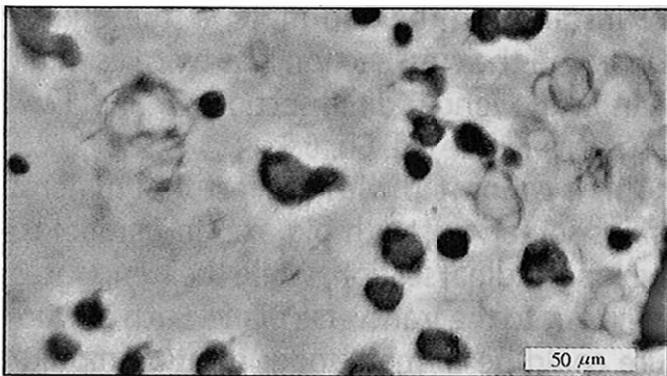


Fig. 6. OM image of the porcelain microstructure of an unknown, probably Russian manufacturer from the turn of the 19th and 20th centuries. Round black pores on the background of glassy-mullite matrix and quartz grains with peripheral cracks on glass edges, are visible. A few dark areas reflect chipped off quartz grains

The homogeneity of the body of the examined porcelain from the late 19th century or the turn of the 19th/20th century can be assessed as quite good in micro scale. The content of residual quartz was low and equal to about 10%. Observed grains had size of  $5 \div 40 \mu\text{m}$ . Larger grains were not observed and all quartz relics were strongly melted. They had wide rims of melted  $\text{SiO}_2$  (Fig. 5) and were sufficiently connected with matrix. However, part of quartz relics contained peripheral cracks or were chipped off during the preparation of the microsection of the old porce-

lain sample (Fig. 6). The porosity was relatively high – about 9%. Round and well-developed pores were as a rule between 5 and  $25 \mu\text{m}$  (calculated average value –  $9.3 \mu\text{m}$ ). The glass and mullite phases constituted about 81%. It was impossible to determine accurate content of the mullite phase, especially of primary mullite. Nevertheless, needle secondary mullite was numerous. Only in form of precipitates accounted for at least 22%. Precipitates significantly varied in size – from about 10 to over  $40 \mu\text{m}$ , and were obviously very well connected with the glassy phase. The content of the glassy phase in the material can be only estimated and constitutes less than 60%. The degree of sintering of the material is high and even a slight overheating of the shard took place. This was expressed in the structural picture of the phases. As a result of dissolution, decreased content of quartz. Quartz grains became smaller, with rounded edges. Glass edges around them expanded. The content of needle secondary mullite increased, as well as the size of the pores, which have a round, well-developed shape.

As has been mentioned, comparative tests were performed on a typical sample of contemporary porcelain of foreign production. The test sample was taken from a cup that has been intensively used for several years. Image of the material microstructure with colour marking of the individual phases in the ceramic body is shown in Fig. 7. Inspection of the porcelain microstructure of the cup indicated the correct degree of firing.

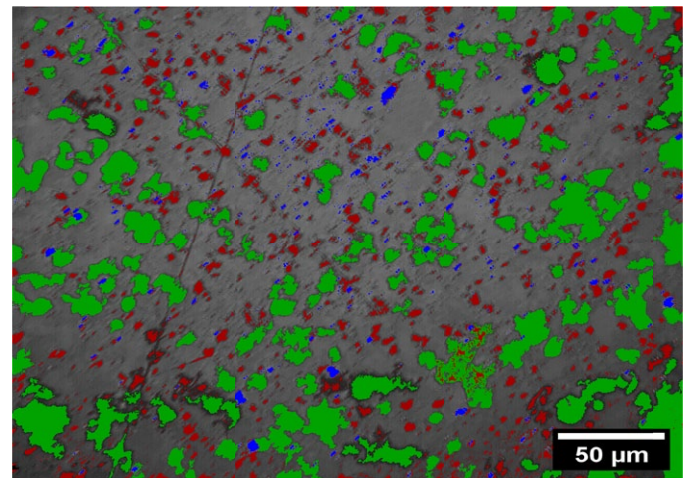


Fig. 7. Image OM of the microstructure of contemporary porcelain of the heavily used cup. Individual phases marked with colours. The quartz phase, most of which was chipped off, was marked in green, pores – in red, cullet particles – in blue. Glassy-mullite matrix constitutes a grey background.

The material showed good homogeneity and typical phase composition. Quartz (green in Fig. 7) accounted for about 15% of which, however, a large part of the grains were chipped off. Relics were usually  $5 \div 30 \mu\text{m}$  in size, larger grains were rarely found – up to  $80 \mu\text{m}$ . Majority of relics were crushed out or contained peripheral cracks. High degree of damage in the quartz phase indicate clear aging processes, related to quartz stresses and associated with the intensive use of the cup for several years. The material contained a small amount of cullet

(blue in Fig. 7) – likely within 1 – 3%, with some fragments probably chipped off. The porosity of the shard was typical and amounted to 5 – 6%. The pores (red in Fig. 7) had a size of a few, rarely a dozen or so micrometres. Glassy-mullite matrix constituted approximately 78%. The mullite precipitates were almost indistinguishable from the grey matrix and the mullite phase content could only be estimated at about 20%. The precipitates had approximate size of  $10 \div 40 \mu\text{m}$ , were distributed with good homogeneity and were very well bound to the matrix. The content of the glassy phase could be assessed at less than 60%. In general, it should be stated that the contemporary material does not show any significant differences in relation to the historic porcelains. The identified aging effects are related to the intensive use of the vessel (repeatedly pouring of boiling water).

As a reference to the ceramic whiteware materials presented above, tests were carried out on typical (electro)technical quartz porcelain. The image of its microstructure is shown in Fig. 8. The composition of raw materials of technical porcelain – C 110 type [17] – was typical and comprised around 35% of kaolins, about 20% of refractory plastic clays, less than 20% of quartz sand and feldspar fluxes – round 25%. Sometimes a few percent of cullet is also added.

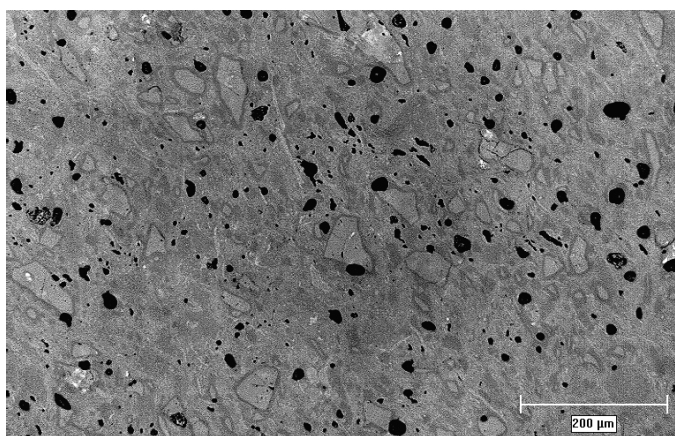


Fig. 8. Image OM of the microstructure of typical technical porcelain, magnification 100 $\times$ . Brighter relics of quartz and darker precipitates of mullite against the background of gray glassy matrix are visible. Black cavities remaining after the crushed out quartz grains occupy around 6% of the surface. Small pores cover approximately 0.5%

The microscopic phase analysis of technical porcelain sample (the insulator material) revealed generally sufficient homogeneity in semi-macro and micro scales. The content of quartz was equal to  $20 \pm 2\%$ . Dominated fraction of the size of dozen or so micrometres, but also a significant portion accounted the relics in the range of  $20 \div 30 \mu\text{m}$ . Part of quartz relics contained cracks and was insufficiently connected with matrix. In consequence a noteworthy amount of quartz grains fell out during the preparation of the microsection of the tested sample. Mullite phase in the form of precipitates constituted  $22 \pm 3\%$  of the material. Precipitates were relatively small, mostly about  $10 \mu\text{m}$ . They were very well connected with the glassy phase, quite densely and uniformly distributed in it. The porosity was

low – about 0.5%, the pores were round and had a size of several micrometers. The content of the glassy matrix in the material amounted to  $55 \pm 4\%$ . It is the high quantity as compared to other (electro)technical porcelain materials. The material contained also small amount of cullet from grinding media. It should also be emphasized, that the content of quartz in various other (electro) technical C 110 type porcelains, which were microscopically examined for many years by the first author of the work, as a rule was at least 20%. In extreme case, however, it reached even up to 41% [15].

#### 4. Discussion

All three historic porcelains show the typical microstructure characteristic of hard porcelain. The homogeneity of their shards can also be regarded as correct. Both their microstructure and phase composition are very similar to typical contemporary whiteware materials [3,13,15,19], including also tested as a reference present porcelain. Although the phases occurring in historical materials are completely typical, their content shows significant differences. This is not only due to the diverse raw materials used by different manufacturers. This is either a consequence of differences in the sintering degree. Only the first and oldest of the historic materials (early 19th century) showed basically correct firing. The second one, probably German, was slightly underburned, while the third porcelain (probably Russian) was slightly overheated.

The degree of firing affected the number and shape of the quartz grains and the thickness of the quartz rims around the grains, the content of the mullite phase (especially needle secondary mullite) and the parameters of shard porosity. The glass content in all tested materials was very similar – about 60%, only slightly lower in (electro)technical porcelain (ca 55%). Quartz usually constituted a dozen or so percent of shards (10-16%). Its amount and grain size decreased with the degree of shard firing. Then the thickness of rims of melted  $\text{SiO}_2$  around the quartz grains also increased. The glassy-mullite matrix constituted about 80%, of which around 20% was mullite, in particular needle secondary. These contents were a few percent lower in the case of underburning and slightly higher if overburning (about 2-4%). This effect is known and described in the literature [3,13,15,19]. The pores (of course – only closed ones) constituted less than 10%. The better the body was fired, the better the pores were developed and usually larger (typically from a few to about  $25 \mu\text{m}$ ).

It should be emphasized that in the case of slightly underburned material, (probably German, 19th century), amplified aging processes were found, related to quartz stresses. Grains had internal cracks and were insufficiently connected with matrix. In the vicinity of some quartz grains, small cracks passing into the material matrix were observed. In the case of the other historic porcelains, the aging processes were very restricted and limited to peripheral cracks around the quartz grains. Clear degradation of contemporary material was related to the intensive use of the

vessel for several years (repeatedly pouring of boiling water).

The (electro)technical porcelain tested in this work was a typical representative of the C 110 type quartz materials [15,17,18]. Its microstructural composition, content and parameters of individual shard-building phases can be considered representative of insulating materials of this class [3,15,20]. Compared to the other tested whitewares – historic and present – the (electro)technical material shows clear differences. The content of quartz was much higher – about 20%, and in the materials of this type it can be even higher. Quartz grains are of different sizes, most often they are a dozen or so micrometres and have pronounced rims of melted SiO<sub>2</sub>. With a very similar content (about 22%) and parameters of the mullite phase, there is clearly less glass (about 55%). However, in (electro)technical porcelains it is usually even less glass phase. Due to performance requirements, the porosity is an order of magnitude lower than that of whitewares. Differences in the microstructural arrangement of shard are a consequence of adapting the composition and technology of (electro)technical materials to operational requirements and are not surprising. It should also be added that the insulating porcelains (quartz and aluminous) are characterized by a “flowing river” fracture, different from the typical – shell and are not translucent [15,21]. However, they make a specific sound when hit.

In the case of semi-vitreous porcelain (so called porcelit), the raw material composition basically does not differ from the classic hard porcelain. The difference lies in the introduction of a less noble raw material in place of kaolins – brightly burning refractory clays. They are less refractory than kaolins and contaminated with admixtures lowering the sintering temperature. At the temperature of 1250-1280°C, a material with the appearance of porcelain is obtained and its water absorption is usually within one percent. Significantly lower purity of the raw materials, combined with a lower sintering temperature, makes the shard not translucent and it has low whiteness. The phase composition is similar to porcelain, but apart from a significant typical – closed porosity, there is open porosity (usually small), the quartz content is higher – about 20% and with a significant amount of mullite (largely primary) there is less glassy phase – around 45% [3].

### 5. Concluding remarks

As part of the presented work, 5 porcelain materials were tested, including 3 historical and one (electro)technical. Generally similar parameters of microstructure and phase composition were found for all tested materials. Clearer differences occurred only in the case of (electro)technical porcelain. However, this is related to adapting the composition and technology of (electro)technical materials to operational requirements and is no surprise.

Research has shown that historical porcelains from the 19th century do not show any major differences in comparison with typical contemporary material. It is noteworthy, however, that there took place a slight underburning of the material probably

of a German producer and a slight overheating of the shard of probably Russian-made porcelain. This affected the quartz content, which usually constituted a dozen or so percent. However, its amount and size of grains decreased with the degree of shard firing. At the same time the thickness of rims of melted SiO<sub>2</sub> around the quartz grains grew. Moreover the content of glass-mullite phase (about 80%, including around 20% of mullite) was a few percent lower in the case of underburned German material and slightly higher in the overheated Russian one. The porosity of the tested historical porcelains was similar and ranged from 7 to 9%. Only the oldest porcelain material, of unknown manufacturer (early 19th century), showed a medium degree of sintering, that can be considered correct.

For all tested materials, it was found that smaller or larger amount of quartz relics contained peripheral cracks or were chipped off from the microstructure of the shard. This means the presence of quartz stresses, which are a factor adversely affecting the compactness and durability of the material. In the case of underburned German porcelain a significant degree of damage in the quartz phase indicate clear aging processes. In the vicinity of some quartz grains, small cracks passing into the material matrix were observed. Therefore underburning can intensify degradation processes. Nevertheless, in the case of the other tested porcelain materials, the degradation processes were limited and consisted of a more or less weakened connection between the quartz grains (sometimes cracked) and the glassy phase. Only in case of contemporary material clear degradation effects were related to the intensive use of the vessel – repeatedly pouring of boiling water for several years.

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